Adsorption of Phenols from Different Solvents on Graphene: Semi-Empirical Quantum Mechanical Calculations

Pablo Húmpola[1], Héctor S. Odetti[1], Alberto G. Albesa[2] and José L. Vicente[2,*] *(1) Cátedra de Química Inorgánica, Facultad de Bioquímica y Cienicas Biológicas, Universidad del Litoral, CC242 (3000), Santa Fe, Argentina. (2) Departamento de Química, Facultad Ciencias Exactas, UNLP, Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CC 16, Suc. 4 (1900) La Plata, Argentina.*

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ABSTRACT: The adsorption of phenol from aqueous solutions on carbon surfaces is discussed from different theoretical points of view, such as Monte–Carlo simulations, semi-empirical calculations, density functional theory and molecular dynamics. We performed a quantitative analysis of the adsorption of aromatics in general, and phenolic compounds in particular, through semi-empirical quantum mechanical calculations using different approaches. Our results raise doubts that phenol is primarily adsorbed in flat position on the graphene layers, and consequently whether the adsorption forces are controlled by π–π dispersion interactions between the aromatic ring of phenol and the graphene layer structure. Based on the results of quantum mechanical calculations (carried out through various approaches), we conclude that neither surface oxidation nor the presence of a polarizable solvent is consistent with the claim that π–π interactions are dominant in the adsorption of phenolic compounds on graphite.

1. INTRODUCTION

The adsorption of organic substances from dilute aqueous solutions at the surface of solid materials is determined by the properties of adsorbate, solvent and adsorbent. Because carbon has a high adsorption capacity for organic compounds, it is the most commonly used adsorbent for removing such compounds from aqueous media (Carrott and Carrott-Ribeiro 1996; Hugi-Cleary and Stoeckli 2000). However, this type of adsorption is a complex process and there still exists considerable difficulty in fully explaining the results of adsorption studies. The main cause of this difficulty results from the large number of variables involved. Adsorbate chemical nature, solubility, molecular size and shape, type of functional groups, dissociation, association and salvation effects are the main factors influencing adsorption. The porous structure, adsorption capacity and chemical character of surface groups characterize adsorption properties of a solid surface. Beyond the global vision of these aspects reported by Dabrowski *et al*. (2005) and Mourao *et al*. (2006), the presence of other competing solutes and solvent molecules, as well as the ionic strength and pH of the solution that determine the solid surface charge, may affect the adsorption dramatically. The complexity of adsorption process from a liquid phase makes its theoretical description very complicated (Everett 1973; Brown and Everett 1975; Everett and Podoll 1979; Davis and Everett 1983; Jaroniec 1983; Derylo-Marczewska and Jaroniec 1987;

*Author to whom all correspondence should be addressed. E-mail: vicente@inifta.unlp.edu.ar (J. L. Vicente)

Jaroniec and Madey 1988; Enfremenko and Sheintuch 2006; Terzyk *et al*. 2010). However, its practical importance, i.e. in environmental protection, wastewater treatment or some other technological processes, increases the interest in this phenomenon. In many theoretical descriptions, the effect of various factors on liquid adsorption was investigated separately. By contrast, these effects may mutually compensate themselves. Thus, it is very difficult to exactly evaluate the influence of heterogeneity, lateral or electrostatic interactions separately. It seems to be reasonable to estimate the global non-ideality of the adsorption system instead (Marczewski *et al*. 1986; Derylo-Marczewska 1995).

Functional groups and delocalized electrons of the graphitic structure determine the apparent chemical character of an activated carbon surface (Everett 1973). Oxygen, for example, may be present in various forms, such as carboxyl, carbonyls, phenols, lactones, aldehydes, ketones, quinines, hydroquinones, anhydrides or ether structures. These groups may also interact among themselves. Some groups, such as carbonyl, carboxyl, phenolic, hydroxyl and lactonic, are acidic, whereas pyrone, chromene, and quinine are basic (Brown and Everett 1975).

The presence of water further modifies the chemistry of a surface, as its interaction with the specific groups on the carbon surface may modify their chemical behaviour. Because of the amphoteric character of a carbon surface, i.e. to the acidic and/or basic functional groups, the surface properties may be influenced by the pH value of the co-existing bulk liquid phase. Thus, when a dissolved chemical species that is to be removed (e.g., by adsorption) has an acidic and/or basic character, the acidic or basic sites on the carbon may also participate in the interaction.

Among the organic substances, the adsorption of phenol from aqueous solutions onto carbons has received, in particular, a great deal of attention, and an exhaustive review has been published previously (Radovic *et al*. 1997, 2000). Currently, the underlying mechanism and the prediction of adsorption equilibrium remain open questions, although a number of models have been proposed. It appears that the pH of the solution, the real surface area of the solid and functional groups play a major role.

Three kind of interactions, between the carbon surface and the phenols, have been initially proposed, namely, (i) electron donor–acceptor interactions between the aromatic phenolic ring and the surface oxygen groups, (ii) dispersion effect between the aromatic phenolic ring and the π electrons of the graphitic structure, (iii) electrostatic attraction and repulsion when ions are present, but if adsorption takes place from unbuffered solutions, all the three types of surface–phenol interactions may occur simultaneously (Dabrowski *et al*. 2005).

Although everything seems to indicate that the physical adsorption occurs as a result of dispersive interactions between the aromatic part of the phenol and the carbon basal planes (Salame and Bandosz 2003), other researchers have suggested that aromatic compounds adsorb on carbons through a donor–acceptor complex mechanism (Terzyk 2003), with the carbonyl oxygen of the carbon surface acting as the electron donor and the aromatic ring of the adsorbate acting as the acceptor. Once the carbonyl groups are exhausted, the aromatic compounds form donor–acceptor complexes with the rings of the basal plane. Thus, owing to the oxidation of carbonyl groups to carboxyl groups, there is a decrease in phenol uptake after carbon oxidation. As a result, the electron donor–acceptor complexes cannot be formed. Despite these opinions, today it is accepted that this donor–acceptor complex mechanism is not the driving force for the adsorption of aromatics on activated carbons (Moreno-Castilla 2004).

Some years ago (Coughlin and Ezra 1968), Coughlin and Ezra pointed out that ‘evidence for any single explanation (of the decrease of phenol uptake with increase in surface acidity) is not overwhelming’, but ‘it is hoped that continuing research will shed more light on this question’. However, many times this was not the case, for example, Dabrowski *et al*. (2005) reported that the effect of carbon–surface chemical composition on adsorption of phenol decreases with the rise

in temperature, and at the same time (Salame and Bandosz 2003), other authors claimed that at higher temperatures the effect of surface chemistry becomes more pronounced.

Parallel to the experiments mentioned in the preceding text, there have been various attempts to try to explain these behaviours using theoretical simulations on models that simulate such complex systems (Terzyk *et al*. 2010). From the point of view of substrate models, they do not often take into account the connectivity of the pores, or curvature, or tortuosity, and the defective graphene segments shown in transmission electron microscopy and in X-ray studies (Albesa *et al*. 2012). From the standpoint of the 'solvent effect', linked to the presence of surface functionalities, the important role played by water, should be contrasted with that of other solvents (Mahajam *et al*. 1980; Moreno-Castilla 2004).

For the quantitative analysis of these views on the adsorption of aromatics in general and particularly on phenolic compounds, in the present paper we perform semi-empirical quantum mechanical (SQM) calculations through three different approaches. First, we discuss the geometric and energetic aspects of the adsorption of rigid phenol molecules on the graphite surface through the results of computer simulations in the grand canonical Monte–Carlo (GCMC) approach. Second, we use the PM3 method to describe the interaction between different phenolic compounds and oxidized graphene (OG) surfaces, checking the results with density functional theory (DFT) calculations. In this case, the substrate is emulated using a coronene molecule. Finally, we perform the calculations on the DFT formalism, in which the presence of different solvents is incorporated (using the polarizable continuum model or PCM). In some of these systems, we also carry out molecular dynamic simulations.

2. AROMATIC MOLECULES ON GRAPHENE SURFACES, GEOMETRIC AND ENERGETIC ASPECTS

From the theoretical point of view, the complexity of the adsorption of aromatic molecules (AMs) on carbon surfaces required a systematic analysis of all elements involved. For any calculation of the interaction between a solid and an AM, it is necessary to make a model that describes both the substrate and the molecule. As a first example, we consider a graphite substrate.

From the substrate side, to calculate the interaction between each particle (atom) constituting the AM and the solid, the Steele's 10–4–3 potential is frequently used, in which the interaction parameters can be obtained using Lorentz–Berthelot combining rules. This potential can also include a corrugation factor to consider the periodic variation on the surface. The extreme case is the exact description, with the complexity that requires the quantum mechanics' description of the semi-infinite arrays of carbon atoms. The intermediate situation is an SQM model for the AM–graphite interaction, in which the graphite surface is represented by a planar polyaromatic molecule (coronene), because of the similar chemical characteristics. The calculation can be performed using PM3 semi-empirical methods. Figure 1 shows a typical case.

From the molecule side, the first approach that is usually used is to assume that it is spherical. Although this approach is not entirely correct, in many cases acceptable results are obtained from theoretical simulations. However, the degree of theoretical and computational simplicity achieved by this kind of approach leads to loss of information regarding orientation effects produced in the adsorbate on the surface of the solid. This is particularly relevant when the adsorbate is polyatomic. The extreme case of the exact solution is obviously highly complex, because it involves the use of quantum mechanical descriptions of the adsorbate molecules, the solid and their respective interactions. The intermediate situation consists in assuming that molecules are rigid, and every atom is a centre or site of interaction. This makes it possible to analyze the effects

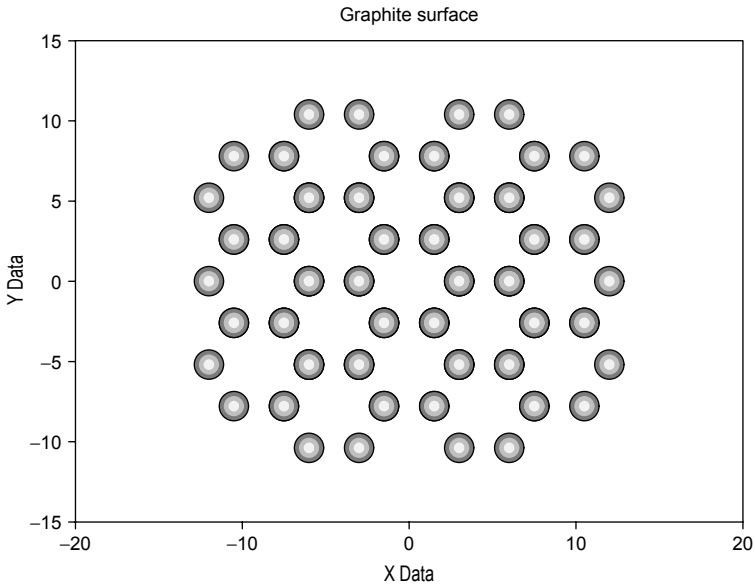

Figure 1. Planar polyaromatic molecule that mimics a graphite surface.

of the relative orientation between the adsorbent and adsorbate. These calculations can be performed by using the AM1 method (standard methods of calculation, such as Gaussian, are available in most commercial software). This ensures that the structure of the AM used in the simulations reproduces both the geometry and the electrostatic interactions. Another situation is optimizing the molecular configurations using the PM3 method to describe interactions (for calculation purposes, there are different commercial software available, such as HyperChem). In these cases, results can also be checked with DFT calculation using the PW91 functional for the exchange and correlation within a small-set basis of the phenol molecule.

Here we discuss different results that can be obtained by combining different kinds of approximation, from both the substrate side and the molecule side. As a first example, we discuss the case of the phenol on graphite, when AMs are considered rigid, with their parameters obtained using the AM1 method and their interaction with the substrate calculated through the Steele's potential 10–4–3 (Bertoncini *et al*. 2002). Phenol physical adsorption was then studied by means of computer simulations with the GCMC method. The graphite surface offers domain adsorption sites located at the centre of the carbon hexagon (centre) and between two carbon atoms (saddle). The interaction energy between adsorbed molecules was calculated by taking into account the electrostatic energy. The dispersion energy contributions were obtained with a Lennard-Jones potential (6, 12). Gas solid-energy fluctuations are mainly due to oxygen carbon (graphite) contribution. Lateral interaction energy is attractive due to the electrostatic component of O–H and C–H pair interactions. Moreover, C–H almost compensates for H–H repulsive interaction. The relative orientation of phenol molecules is explained on the basis of the interaction potentials. In principle, there is no evidence that the dipole moment of the phenol molecule causes any special effect or determines the structure of the adsorbed film. Interaction of phenol with graphite is not strong enough to form a regular structure at least in the temperature range studied (250–350 K). The net orientation of phenol on the surface shows equilibrium between lateral and gas–solid energies.

The total energy tends to 25–30 kJ/mol at the multi-layer limit, and this value is smaller than the vapourization enthalpy. The estimated heat of adsorption, at zero coverage, was 35 kJ/mol.

When two layers are completed, the total adsorption energy is 50% lateral interaction. From the adsorption isotherms obtained in the GCMC algorithm, the adsorbed layer did not show any order even at the lowest temperature studied. The layer thickness was estimated at 0.744 nm. The distributions of molecules with respect to the lateral interaction energy showed that they are almost temperature independent.

3. EFFECT OF SURFACE GROUPS

Some carbon properties, as adsorbent, are based on its chemical composition. In graphite, with a highly oriented structure, adsorption occurs primarily through the dispersive component of the van der Waals forces. However, the imperfect arrangement of graphene in activated carbons causes the appearance of unsaturated valences and unpaired electrons that are responsible for high affinity for polar or easily polarizable molecules. This disorder also causes an increase in the amount of heteroatoms (oxygen, hydrogen, etc.). The presence of surface groups consisting of hydrogen and oxygen in molar proportions of up to 30% and 15%, respectively, is common and produces significant changes in the properties of activated carbon as adsorbent. These groups may come with the original material, or may be introduced during the activation process or during the treatment of the sample after activation.

Oxygenated groups are by far the most important to define the surface characteristics and behaviour of an activated carbon as adsorbent. At the edges of graphene, where the plane ends, there are atoms with unsaturated valences and the unpaired electron concentration is large. In the case of graphite, the ratio of edge atoms is very low with respect to the plane, and therefore the adsorption of oxygen is very low. By contrast, in microcrystalline carbons (non-graphitizable) such as activated carbons, there is much higher proportion of edge atoms and, therefore there is a higher adsorption capacity for oxygen.

The nature of surface groups has been studied in detail with the help of spectroscopic techniques. Today there is an agreement on the following points:

- Introduction of acidic surface groups causes the π electrons to be removed from the carbon matrix and those electrons enhance phenol adsorption through dispersive interactions; their removal results in a decrease in the average energy of the adsorption sites (Salame and Bandosz 2003).
- Oxidation causes an increase in the number of carboxylic groups; the physical adsorption is affected by weaker interactions between the benzene ring of phenol and the carbon basal plane (Moreno-Castilla 2004).
- The carboxyl groups inhibit the adsorption of phenol and increase the affinity of carbon towards water, and the solvent molecules block some micropores. This effect is explained by phenol adsorption that is governed by 'π–π dispersion interaction' between the basal plane of carbon and the aromatic ring of the adsorbate. Oxygen bound to the graphite edges localize electrons and, thereby, remove them from the π-electron system of the basal plane. Consequently, the π–π interaction is weakened (Dabrowski *et al*. 2005).

If one intends to describe the interaction between AMs and a solid substrate, the actual characteristics of both must be considered. From the viewpoint of the substrate, whether it is an activated carbon or not, it is necessary to take into account the presence of surface groups, because the increase of surface acidity, due to oxidation, decreases the amount of adsorbed AMs from aqueous solutions (Radovic *et al*. 1997, 2000). Of course, the representation of the substrate as a stack of pure graphite layers does not take into account this situation. One way to overcome this

shortcoming, and consider the interactions in more detail, is to replace the substrate using clusters of AMs (Albesa and Vicente 2008). Using semi-empirical methods, Tamon and Okazaki determined the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of an aromatic-model cluster without substitution; using the same cluster, but with additional phenolic and carboxylic groups, they found that groups that accept electrons (carboxylic) decrease the HOMO and LUMO levels, whereas groups that provide electrons increase the levels with respect to the original cluster (Tamon and Okazaki 1996).

We studied these systems by the PM3 method to describe the interaction between AMs and OG surfaces, using HyperChem (HyperChem 2002) for the calculations. The results were also verified with DFT calculations, using the PW91 functional for the exchange and correlation, within a small-set basis for the phenol molecule and using a coronene molecule as substrate. Calculations showed a good agreement with the results obtained from PM3. Figure 2 shows the AMs used and Figure 3 shows the corresponding surfaces. Geometries of the OG–AM complexes were optimized using a gradient of 0.001 Kcal/A. The interaction energy ΔE was calculated from equation (1) as follows:

$$\Delta E = E(OG–AM) – [E(OG) + E(AM)] \quad (1)$$

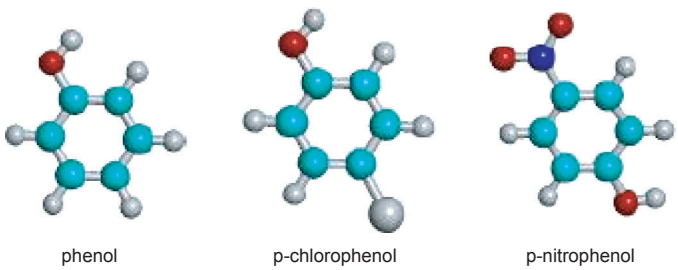

Figure 2. Aromatic molecules used in the study: phenol, *p*-chlorophenol and *p*-nitrophenol.

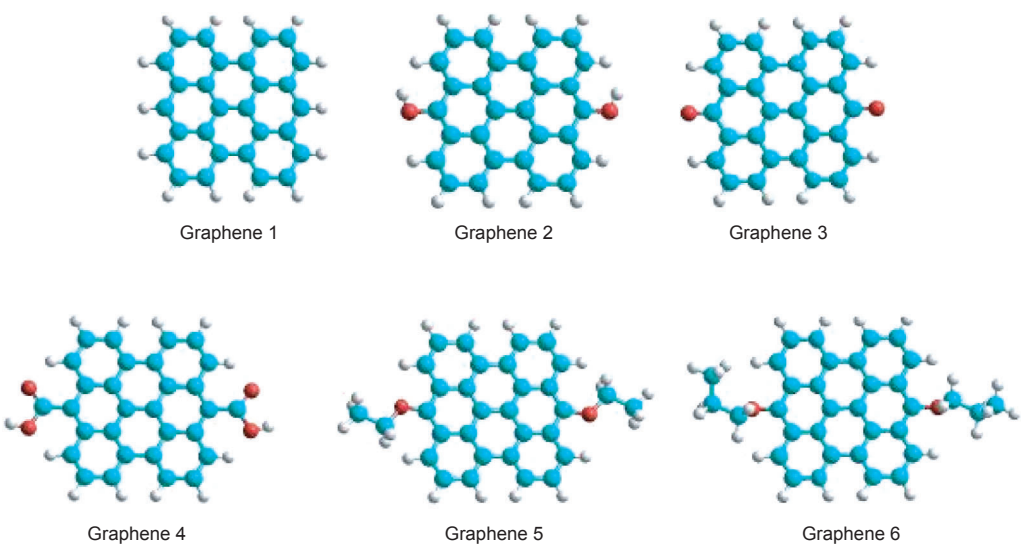

Figure 3. The six graphene surfaces used in the study. Red atoms represent oxygen.

where E(OG–AM), E(OG) and E(AM) are the energy of the complexes, the OGs and the AMs, respectively.

In Figure 3, Graphene 1 (G1) corresponds to a clean surface (without any surface group), and the rest of the surfaces, from Graphene 2 (G2) to Graphene 6 (G6), correspond to AC–OH, AC–O, AC–COOH, AC–OC2H5 and AC–OR, respectively. In Table 1, we show the interaction

TABLE 1. Calculated Energies for Different Complexes

KJ/mol	Phenol	*p*-Chlorophenol	*p*-Nitrophenol
Graphene 1	–1.89	–2.13	–2.89
Graphene 2	–1.88	–2.12	–3.10
Graphene 3	–1.16	–4.29	–2.16
Graphene 4	–1.94	–2.18	–2.78
Graphene 5	–2.79	–1.86	–3.80
Graphene 6	–2.31	–2.20	–2.88

energy resulting from equation (1). From our calculations, in the case of phenol, we did not observe significant differences in the adsorption energy because of the presence of acidic surface oxygen groups, which would be due to the removal of π electrons from the basal plane, assuming that the interaction of these electrons with π electrons of the phenol aromatic ring governs the process of adsorption. Perhaps this could happen if there were more of these groups at graphene edges, or more phenols competing for π electrons of the basal planes. The case of carbonyl groups, by contrast, is quite different, because according to the calculated energies, there is a clear advantage of phenol adsorption in the presence of these surface groups (G5). According to Mattson and co-workers, this could be because phenol adsorbs on carbons by a donor–acceptor mechanism, with the carbonyl oxygen of the surface acting as the electron donor and the aromatic ring of phenol as the acceptor, without considering that carbonyl groups can evolve into carboxyl groups by surface oxidation, taking into account that G5 is a basic surface. We can compare the behaviour of phenol, nitrophenol and chlorophenol if we follow the analysis about the formation of electron donor–acceptor complexes, with the aromatic ring of the phenolic compounds on basic sites of the surface of carbons, which predominate when the oxygen content is low. Taking into account that the increase in surface basicity of activated carbons favours the formation of these complexes, which results from a concomitant increase in the value of the relative affinity, if we compare the changes in adsorption energy between G5 and G1 with the different phenolic compounds (see Table 1), we can observe that they have the same order of relative affinity:

$$\text{phenol} < p\text{-nitrophenol} < p\text{-chlorophenol}$$

The general trend is that as substrate basicity increases, the interaction energy increases. The order for the adsorption capacity follows the increase of sample basicity, G2 > G3 > G4 > G5 > G6. In other words, the most basic cluster presented the best mechanism for the adsorption of aromatic compounds observed, which is in agreement with experimental results taken from the literature (Villacañas *et al*. 2006).

After geometry optimization, one finds that the preferred configuration is when AMs are oriented as a T, forming an angle of 90° with the graphene surface. The –OH groups of phenol and

p-chlorophenol molecules are oriented forming an angle of 30° with the graphene surface. Nitrophenol molecules show a competition between the groups $–NO_2$ and –OH, and the orientation is similar to that of phenol on the substrates Graphene 2, Graphene 5 and Graphene 6, but with different adsorption sites, while in other cases, the orientations are with the choice of the group $–NO_2$ interacting with the edges of the surface (as with nitrobenzene).

The configuration reached between the molecules and clusters modelled does not promote the π–π dispersion, which leads to the conclusion that this would not be the only interaction present. For these systems, the PM3 method provides a low-cost computational tool that produces results of the same order as DFT methods showing good agreement with experimental data, in cases where this information exists.

There are two experimental results that do not agree with our conclusions. First, also in the absence of carbonyl groups, the adsorption of phenol from aqueous solutions is affected by other surface groups (assuming normal 'oxy' conditions, when oxygen content is not low), and second the presence of carboxyl groups has been proved to really reduce phenol uptake. What elements did we not take into consideration in the calculations? At least one of them, and very important if we are considering very low concentrations of phenolic compounds, is obviously the solvent. We explore this in the 'Effect of the Solvent' section.

4. EFFECT OF THE SOLVENT

Not only phenol but also water molecules are present on the surface of active carbons. Therefore, competition between phenol and water should be taken into account when the adsorption of the former is calculated (Dabrowski *et al*. 2005). Even though our calculation (see the 'Effect of Surface Groups on the Surface' section) does not give relevance to the role played by carboxyl surface groups, inhibiting the adsorption of phenol through the removal of π electrons from the basal plane, we cannot say the same about the adsorption of water.

It was also proposed that the bonding of water molecules to the oxide functional groups by H bonding can play an important role in the uptake of phenolic compounds. In the previous the section, we have considered the presence of carbonyl groups on carbon in a context of a basic behaviour of the surface, but if there is an oxy condition (perhaps by the presence of water), the oxidation of carbonyl groups to carboxyl groups inhibits the formation of donor–acceptor complexes, as was suggested by Mattson and co-workers (Mattson *et al*. 1969). In addition, water is very sensitive to the presence of acidic surface groups; the bonding of water molecules to the oxide functional groups by H bonding is well known (Coughlin and Ezra 1968), and therefore water molecules adsorbed to oxygen groups become secondary adsorption centres, which retain other water molecules by H bonds, and as a result complexes of associated water prevent the migration of phenol molecules to a large portion of surface area.

Summarizing the overall reaction, we conclude that the mechanism of phenol adsorption is determined not only by 'π–π interactions' (Salame and Bandosz 2003) and 'donor–acceptor' complex formation but also by the so-called solvent effect. This usually neglected effect, together with the two above-mentioned effects, occurs simultaneously during adsorption and strongly modifies the adsorption properties of carbon towards phenol. Beyond the constraints that any virtual carbon model has, it is not enough to consider the effects of the solvent alone, that is, considering a single solvent; rather it must also be contrasted with the results obtained using other solvents with different properties, just as the same problem is investigated experimentally.

To verify the scope of the claims made in the previous sections concerning the effect of the surface groups on the adsorption of AMs, one must also take into account the presence of the solvent, and whether it confirms or modifies previous results. We studied phenol adsorption on a cluster of AMs (see Figure 4), modelling the activated carbon surface using different

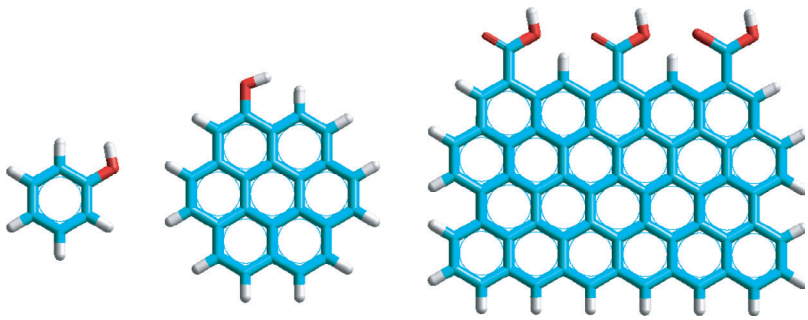

Figure 4. Images of the basic clusters used in DFT calculation and molecular dynamic simulations.

solvents: ethanol, water, hexane, benzene and void. To perform the calculations, we used DFT with PW91 functional, a 6-31G(d,p) basis set and the Gaussian software. Solvents were simulated using PCM.

To analyze solvent effects in an explicit way, we carried out molecular dynamic simulations. Simulations were performed in a rectangular simulation cell, with periodic conditions in the three axes. Activated carbon was simulated by means of three clusters containing three carboxylic functional groups each (see Figure 4). Solvents were water and cyclohexane. The simulation time was 100 ps at 300 K. The temperature was kept constant by coupling a thermal bath to the simulation cell. The time step was set to 0.001 ps. The size of system was 10^3 nm^3.

In the molecular dynamics calculation, the software adds a term to adjust the velocities, keeping the molecular system near a desired temperature. During a constant temperature simulation, velocities are scaled at each time step (Berendsen *et al.* 1984). The energies obtained from the calculations show that as the solvent dielectric constant increases, the interaction energy between the cluster and the phenol molecule decreases (see Table 2), with water and ethanol being the more positive energies.

TABLE 2. Adsorption Energies Calculated by DFT

Solvent	Void	Water	Ethanol	Benzene	Cyclohexane
Adsorption energy (KJ/mol)	–2.86	1.61	1.16	–0.76	–0.84

Although in almost all reported studies, the role played by water was never denied, because through hydrogen bonding the complexes of associated water prevent the migration of phenol molecules to a large portion of the active surface area within a particle of the adsorbent, and this possibility was many times understated. In order to explore this point we also analyzed the residence time of the phenol molecule in the neighbourhood of carboxylic groups (see Figure 5), comparing the results obtained with water and other solvents (e.g. cyclohexane).

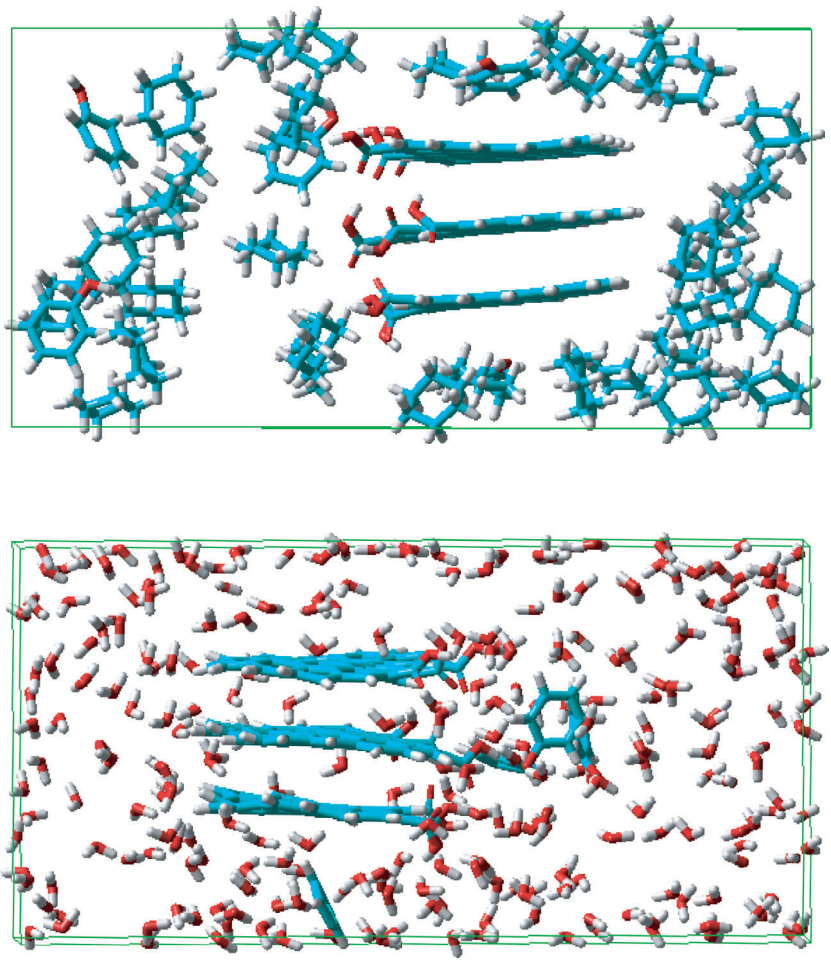

Figure 5. Simulation boxes used in molecular dynamics (to make the figure clearer, some solvent molecules were removed from the box).

In Figure 6, we show the distance between two phenol molecules as function of time for the considered solvents. We can see that in the case of phenol in cyclohexane, it has a greater mobility than in water although residence times are relatively high, which tells us that the type of hydrogen bridge interactions plays an important role in adsorption. This can be due to the great interaction of phenol with water and because water forms hydrogen bridges with carboxylic groups. This would account for the fact that the complexes formed from water inhibit the migration of organic molecules towards a large portion of the active surface area.

As a first approximation, and taking into account that the adsorption is carried out with phenol molecules in parallel position, it could be said that when phenol is adsorbed and forms aqueous solution with a polar solvent, the main mechanism of adsorption would not be π–π interactions, but rather other mechanisms. Although these results do not respond specifically to the question about what the mechanism for adsorption of phenol is, the idea that the interactions are only π–π interactions should be questioned.

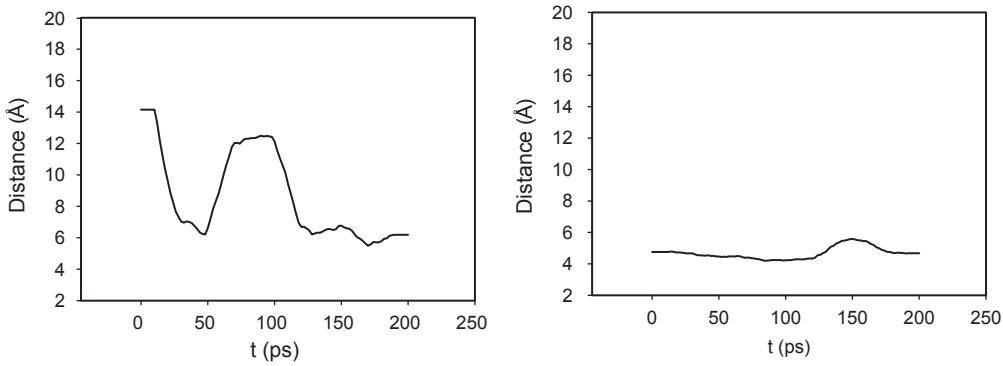

Figure 6. Resident times of the phenol molecule near the activated carbon surface.

5. CONCLUSIONS

To describe the adsorption of organic substances from dilute aqueous solutions on the surface of solid materials, it becomes important to study not only the organic molecule and the solid, but also the whole environment that accompanies this process. For example, it is known that the presence of molecular oxygen has a significant influence on the adsorption capacity of organic substances on activated carbons, due to the appearance of acidic functional groups, which occurs under aerobic conditions, and almost all experimental procedures are carried under these conditions. In spite of the arguments presented about the role of each interaction, nowadays the discussion about which mechanism is of primary importance continues. Of course, almost all authors agree that if adsorption takes place from unbuffered solutions, different types of surface–phenol interactions may occur simultaneously, but the question about the weight that has to be assigned to each one remains without a clear answer.

When studying phenolic compounds, in particular, three kinds of interactions have been proposed, namely, (i) dispersion effect between the aromatic phenolic ring and the π electrons of the graphitic structure, (ii) electron donor–acceptor interactions between the aromatic phenolic ring and the surface oxygen groups and (iii) electrostatic attraction and repulsion when ions are present. Although some authors accept that the decrease in phenol uptake (Terzyk 2003) after carbon oxidation is due to the oxidation of carbonyl groups to carboxyl groups, and as a result, the electron donor–acceptor complexes cannot be formed, today it is argued that the donor–acceptor complex mechanism is not the driving force for the adsorption of aromatics on activated carbons (Salame and Bandosz 2003).

With regard to the proposal in point (i), one can say that if phenol is adsorbed in flat position on the graphene layers, the adsorption driving forces would be due to π–π dispersion interactions between the aromatic ring of phenol and the aromatic structure of the graphene layers. Thus, it has been proposed that acidic surface oxygen groups, which are located at the edges of the basal planes, remove electrons from the π-electron system, creating positive holes in the conducting p band of the graphitic planes (Bertoncini *et al.* 2002). This would lead to weaker interactions between the π electrons of the phenol's aromatic ring and the π electrons of the basal planes, therefore reducing the phenol uptake. However, these arguments have at least two weak points: First, it is assumed *a priori* that phenol is adsorbed in a flat position. Second, the proportion of atoms at the edges is very low compared with the surface atoms, and therefore the adsorption of

oxygen would be very low. Our results, given in the 'Effect of Surface Groups on the Surface' section, also confirm these hypotheses.

Although the second observation may be overcome arguing that, in activated carbons (non-graphitizable), there is a much higher proportion of edge atoms and therefore the oxygen adsorption capacity is also increased, the idea that the molecules are adsorbed in a flat position on the surface goes against the results of quantum mechanical calculations. The relevance of this point is confirmed through the importance that many authors have given to the role the orientation of the molecules on the surfaces plays in the mechanisms of adsorption (Salame and Bandosz 2003).

Our calculations, in the 'Effect of the Solvent' section, show the relevance of the presence of water in the adsorption process, which confirms that when phenol is adsorbed, it forms an aqueous solution with a polar solvent, and the main mechanism of adsorption would not be the π–π interactions, but rather other mechanisms. Although the results do not specifically tell us which one is the basic mechanism of adsorption, it is evident that the π–π interactions cannot play that role. For example, some time before, it was proposed that the adsorption mechanism is by both water H bonding with carboxyl groups and π–π dispersion interactions between the aromatic ring of the adsorptive and the graphene layers. This is because the water molecules, adsorbed on oxygen groups, become secondary adsorption centres, which retain other water molecules by means of H bonds. As a result, the complexes formed from water inhibit the migration of organic molecules towards a large portion of the active surface area.

Finally, based on our SQM calculations, we conclude that neither the oxidation of the surface nor the presence of a polarizable solvent is consistent with the claim that π–π interactions are dominant in the adsorption of phenolic compounds on graphite. We believe that the possibility of a further confirmation of these results will give rise to both new experimental and theoretical challenges. More data from very well–characterized substrates should be obtained and analyzed to search for the role played by the solvent, the pH and temperature. From the theoretical side, new and more detailed models will be required.

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